



## **PAACFIT: a program for analysing positron annihilation angular correlation spectra**

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Danish Atomic Energy Commission  
Research Establishment Risö

# CHEMISTRY DEPARTMENT

PAACFIT: a Program for Analysing Positron  
Annihilation  
Angular Correlation Spectra

by

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## 1. INTRODUCTION

In a measurement of angular correlation of positron annihilation, a spectrum is obtained which in many cases may be assumed to be a sum of central Gaussian curves, symmetrical side-peak Gaussians, and a background. The computer program PAACFIT was developed to perform the analysis necessary to extract the peak parameters from such spectra.

## 2. Mathematical Model of the Spectrum

The measured spectrum is first analysed by the processing and editing code PAAC. This gives an output spectrum

$$(\theta_i, y_i, \sigma_i) \quad i = 1, \dots, n \quad (1)$$

on punched cards, which is fed as input to PAACFIT.  $\theta_i$  are the angles (in mrad); in general they will not be equidistant.  $y_i$  are the counts corrected for background, and  $\sigma_i$  associated standard deviations. We want to make a least-squares fit of a mathematical model

$$f(\theta) = \sum_{j=1}^{k_c} C_j \exp[-p_j^2 (\theta - \theta_0)^2] + \frac{1}{2} \sum_{j=1}^{k_s} S_j \{ \exp[-q_j^2 (\theta - \theta_0 + \omega_j)^2] + \exp[-q_j^2 (\theta - \theta_0 - \omega_j)^2] \} \quad (2)$$

to the spectrum (1). The model has  $k_c$  central peaks and  $k_s$  side peak pairs.  $\theta_0$  is the angular position of the central peaks, and  $\omega_j$  is the angular distance from sidepeak pair no.  $j$  to  $\theta_0$ . The absolute intensity of a central peak is

$$I_j^c = \sqrt{\pi} \frac{C_j}{p_j} \quad (3)$$

and of a sidepeak pair:

$$I_j^s = \sqrt{\pi} \frac{S_j}{q_j} \quad (4)$$

The sharpness parameters  $p_j$  and  $q_j$  are related to the fwhm by

$$\text{fwhm}_j^c = \frac{c}{p_j} \quad \text{and} \quad \text{fwhm}_j^s = \frac{c}{q_j} \quad (5)$$

with  $c = 2\sqrt{\log 2}$ . In particular, (2) degenerates to a sum of central Gaussians if  $k_s = 0$ . Of the parameters in (2),  $\theta_0$  is always adjustable and  $\omega_j$  always fixed. Some or all of the remaining parameters are adjustable, depending on the prescribed constraints (see eq. (13) and (14)).

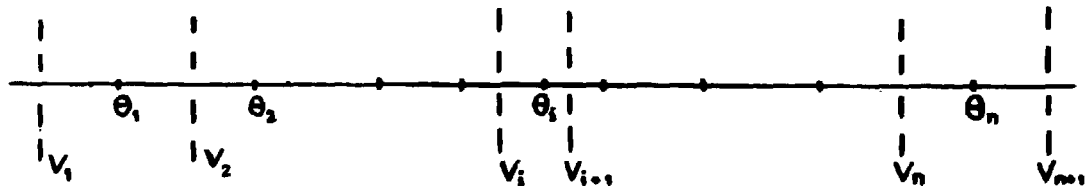
### 3. The Least-Squares Technique

In formulating the least-squares condition, one could compare the  $y_i$  from the spectrum (1) simply to the model value  $f(\theta_i)$  obtained from (2). However, some computational advantages are gained (simpler handling of the constraints (14) and (17) and of the statistics), if we replace  $f(\theta_i)$  by an interval average

$$f_i = \frac{1}{V_{i+1} - V_i} \int_{V_i}^{V_{i+1}} f(\theta) d\theta \quad (6)$$

The new angles  $V_i$  are related to  $\theta_i$  by

$$\left. \begin{aligned} V_1 &= \frac{3}{2} \theta_1 - \frac{1}{2} \theta_2 \\ V_i &= \frac{1}{2} (\theta_{i-1} + \theta_i), \quad i=2, \dots, n \\ V_{n+1} &= \frac{3}{2} \theta_n - \frac{1}{2} \theta_{n-1} \end{aligned} \right\} \quad (7)$$



The expression (6) for  $f_i = f_i(b)$ , which depends on the parameter vector  $b$ , turns out to be

$$f_i(b) = \frac{1}{\Delta V_i} \left( \sum_{j=1}^k \Delta C_{ji} + \sum_{j=1}^k \Delta S_{ji} \right) \quad (8)$$

$\Delta$  is the difference operator with respect to index  $i$ ; further,

$$C_{ji} = \frac{I_j^C}{2} \operatorname{erf} [p_j (V_i - \theta_0)] \quad (9)$$

$$\text{and } S_{ji} = \frac{I_j^S}{4} \left\{ \operatorname{erf} [q_j (V_i - \theta_0 + \omega_j)] + \operatorname{erf} [q_j (V_i - \theta_0 - \omega_j)] \right\} \quad (10)$$

$b$  has  $2(k_c + k_s) + 1$  components;  $k_c + k_s$  intensity parameters,  $k_c + k_s$  sharpness parameters, and  $\theta_0$ :

$$\begin{aligned} & I_1^C, \dots, I_{k_c}^C; I_1^S, \dots, I_{k_s}^S; \\ & p_1, \dots, p_{k_c}; q_1, \dots, q_{k_s}; \theta_0 \end{aligned} \quad (11)$$

According to the least-squares principle we shall find parameters (11) so that

$$\Phi = \sum_{i=1}^n w_i [y_i - f_i(b)]^2 \quad (12)$$

where  $w_i$  are weights of the data points, becomes minimum. The parameters may vary without any restrictions, or, alternatively, constraints of different types can be imposed on them. In this work permissible constraints will be of the following two types:

(a) A fixed value is assigned to one or more of the sharpness parameters  $p$  and  $q$  (or the corresponding fwhm) (13)

(b)  $m$  linear combinations of the (absolute) intensities equal zero ( $m < k_c + k_s$ ) (14)

If we define the relative intensity to be

$$\begin{aligned} i_j^C &= \frac{I_j^C}{I_1^C} \text{ for a central peak} \\ \text{and } i_j^S &= \frac{I_j^S}{I_1^S} \text{ for a sidepeak pair} \end{aligned} \quad \left. \vphantom{\begin{aligned} i_j^C &= \frac{I_j^C}{I_1^C} \text{ for a central peak} \\ i_j^S &= \frac{I_j^S}{I_1^S} \text{ for a sidepeak pair} \end{aligned}} \right\} \quad (15)$$

where  $I$  is the total intensity of all peaks,

$$I = \sum_{j=1}^{k_c} I_j^c + \sum_{j=1}^{k_s} I_j^s \quad (16)$$

then we observe that:

$$\text{relative intensity} = q_l = \text{constant} \quad (l=1, \dots, m) \quad (17)$$

is a set of constraints that is a special case of (b) above. Constraints of type (a) are realized simply by deleting the fixed  $p$  and  $q$  from the parameter list. The vector of adjustable parameters then becomes:

$$b = (I_1^c, \dots, I_{k_c}^c, I_1^s, \dots, I_{k_s}^s, p_1, \dots, p_{k_{cv}}, q_1, \dots, q_{k_{sv}}, \theta_0)^T \quad (18)$$

where  $k_{cv}$  and  $k_{sv}$  are the number of central peaks and sidepeak pairs with variable fwhm, and  $T$  stands for transpose.

Our model (8) is linear in the absolute intensities, but nonlinear in the peak sharpnesses and in  $\theta_0$ . Marquardt's iteration technique <sup>1)</sup> is used in the subspace of nonlinear parameters <sup>2)</sup>. The same method was applied successfully in the program POSITRONFIT<sup>3,4)</sup>, which analyses positron lifetime spectra. The iterations start from a guessed initial set of the nonlinear parameters and are terminated when  $\phi$  has proved to be stationary. A detailed description of the applied ideas is given in an earlier report<sup>2)</sup> that is the basis of the subsequent analysis. The decomposition of the parameter vector in its linear and nonlinear components reads

$$b = \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \text{ with}$$

$$\alpha = (I_1^c, \dots, I_{k_c}^c; I_1^s, \dots, I_{k_s}^s)^T \quad (19)$$

and

$$\beta = (p_1, \dots, p_{k_{cv}}; q_1, \dots, q_{k_{sv}})^T; \quad (20)$$

then the model  $f_i$  (b) is linear in  $\alpha$  and nonlinear in  $\beta$ . The dimension of  $\alpha$  is  $k_\alpha = k_c + k_s$ , and that of  $\beta$  is  $k_\beta = k_{cv} + k_{sv} + 1$ .



Now (8) can be written

$$f_i = \sum_{j=1}^{k_\alpha} \alpha_j u_{ij} \quad (21)$$

with  $u_{ij} = u_{ij}(\beta)$ , and the formulae from the semi-linear least-squares analysis<sup>2)</sup> can be used. Let  $\alpha = \alpha(\beta)$  be the solution of  $\alpha$  conditioned on  $\beta$ , i.e., the  $\alpha$ -vector (cf.(19)) that for a fixed  $\beta$  (cf. (20)) minimizes  $\Phi$ (cf. (12)) under the possible constraints (13), (14), (17). It can be shown<sup>2)</sup> that  $\alpha$  is determined by solution of the linear system

$$\begin{matrix} k_\alpha & m \\ \begin{matrix} C & K^T \\ K & \theta \end{matrix} \end{matrix} \begin{bmatrix} \alpha \\ \mu \end{bmatrix} = \begin{bmatrix} \gamma \\ \theta \end{bmatrix} \quad (22)$$

The submatrix  $C$  has the elements  $c_{jj_1} = \sum_i w_i u_{ij} u_{ij_1}$ , and the vector  $\gamma$  the components  $\gamma_j = \sum_i w_i y_i u_{ij}$ .  $\theta$  is here a zero matrix (or vector).  $K$  contains the  $k_\alpha$  coefficients of each of the  $m$  constraints of type (14); these constraints read  $K\alpha = \theta$ . In the special case (17) the coefficients of  $K$  turn out to be

$$k_{lj} = \delta_{jj_l} - q_l \quad (j=1, \dots, k_\alpha; \quad l=1, \dots, m) \quad (23)$$

$\delta_{ij}$  is the Kronecker delta, and  $j_l$  ( $1 \leq j_l \leq k_\alpha$ ) is the term no. (cf. (19)) associated with constraint no  $l$ .  $\mu$  is the vector of Lagrangian multipliers appropriate for the present constraint-minimum problem; no explicit use will be made of  $\mu$ .

In the nonlinear  $\beta$ - iterations we shall need the quantities

$\frac{\partial f_i}{\partial \beta_j}$ ; as  $\alpha = \alpha(\beta)$ , these can be expressed by

$$\frac{\partial f_i}{\partial \beta_j} = \sum_{j_1=1}^{k_\alpha} \left[ \frac{\partial \alpha_{j_1}}{\partial \beta_j} u_{ij_1} + \alpha_{j_1} \frac{\partial u_{ij_1}}{\partial \beta_j} \right]$$

$$(j' = 1, \dots, k_\beta) \quad (24)$$

Hence, to evaluate  $\frac{\partial f_i}{\partial \beta_{j'}}$ ,  $\frac{\partial \alpha_j}{\partial \beta_{j'}}$  has to be evaluated, and this can be done by taking the derivative of both members of (22) with respect to  $\beta_{j'}$ . The result can be expressed as a matrix equation

$$\begin{matrix} k_\alpha & m & k_\beta & k_\beta \\ \begin{matrix} k_\alpha \\ m \end{matrix} & \begin{bmatrix} C & K^T \\ K & \Theta \end{bmatrix} & \begin{bmatrix} A' \\ M' \end{bmatrix} & = \begin{bmatrix} E \\ \Theta \end{bmatrix} \end{matrix} \quad (25)$$

$A'$  contains the unknown derivatives  $a_{jj'} = \frac{\partial \alpha_j}{\partial \beta_{j'}}$ .  $E$  has the elements:

$$e_{jj'} = \sum_i w_i \left[ \frac{\partial u_{ij}}{\partial \beta_{j'}} (y_i - f_i) - u_{ij} \sum_{j_1=1}^{k_\alpha} \alpha_{j_1} \cdot \frac{\partial u_{ij_1}}{\partial \beta_{j'}} \right] \quad (26)$$

$M'$  contains the derivatives of the Lagrangian multipliers and is not used explicitly. In specializing (26) to the present model, it is practical to introduce some abbreviations:

$$t_i = V_i - \theta_0$$

$$ER_{ij} = \frac{1}{2} \Delta \operatorname{erf} (p_j t_i) / \Delta V_i$$

$$EX_{ij} = \frac{1}{\sqrt{\pi}} \Delta \exp (-p_j^2 t_i^2) / \Delta V_i$$

$$TEX_{ij} = \frac{1}{\sqrt{\pi}} \Delta (t_i \exp (-p_j^2 t_i^2)) / \Delta V_i \quad (27)$$

$$ERS_{ij} = \frac{1}{4} \Delta \left\{ \operatorname{erf} [q_j (t_i + \omega_j)] + \operatorname{erf} [q_j (t_i - \omega_j)] \right\} / \Delta V_i$$

$$EXS_{ij} = \frac{1}{2\sqrt{\pi}} \Delta \left\{ \exp \left[ -q_j^2 (t_i + \omega_j)^2 \right] + \exp \left[ -q_j^2 (t_i - \omega_j)^2 \right] \right\} / \Delta V_i$$

$$TEXS_{ij} = \frac{1}{2\sqrt{\pi}} \Delta \left\{ (t_i + \omega_j) \exp \left[ -q_j^2 (t_i + \omega_j)^2 \right] + (t_i - \omega_j) \exp \left[ -q_j^2 (t_i - \omega_j)^2 \right] \right\} / \Delta V_i$$

The expression for  $u_{ij}$  becomes:

$$j \leq k_c: u_{ij} = \frac{\Delta C_{ji}}{\Delta V_i \cdot I_j^c} = ER_{ij} \quad (28)$$

$$k_c < j \leq k_c + k_s: u_{ij} = \frac{\Delta S_{j_0 i}}{\Delta V_i \cdot I_{j_0}^s} = ERS_{ij_0} \quad (j_0 = j - k_c)$$

The expression in brackets in (26),  $h_i$ , can now be evaluated.  
We find:

$$1) j \leq k_c, j' \leq k_{cv} \quad (29)$$

$$h_i = TEX_{ij'} \left[ \delta_{jj'}, (y_i - f_i) - \alpha_j - ER_{ij} \right]$$

$$2) j \leq k_c, k_{cv} < j' \leq k_{cv} + k_{sv} \quad (j'' = j' - k_{cv}) \quad (30)$$

$$h_i = - \alpha_{k_c + j''} ER_{ij} TEXS_{ij''}$$

$$3) j \leq k_c, j' = k_\beta$$

$$h_i = - \beta_j EX_{ij} (y_i - f_i) + ER_{ij} \left\{ \sum_{j_1=1}^{k_c} \alpha_{j_1} p_{j_1} EX_{ij_1} + \sum_{j_1=1}^{k_s} \alpha_{k_c + j_1} q_{j_1} EXS_{ij_1} \right\} \quad (31)$$

$$4) k_c < j \leq k_c + k_s \quad (j_0 = j - k_c), j' \leq k_v.$$

$$h_i = - ERS_{ij_0} \alpha_j - TEX_{ij'} \quad (32)$$

$$5) k_c < j \leq k_c + k_s \quad (j_0 = j - k_c), \quad k_{cv} < j' \leq k_{cv} + k_{sv} \quad (j'' = j' - k_{cv})$$

$$h_i = \text{TEXS}_{ij} [ \delta_{j_0 j} (y_i - f_i) - \alpha_{k_c + j} \text{ERS}_{ij_0} ] \quad (33)$$

$$6) k_c < j \leq k_c + k_s \quad (j_0 = j - k_c), \quad j' = k_{cv} + k_{sv} + j''$$

$$h_i = -q_{j_0} \text{EXS}_{ij_0} (y_i - f_i) + \text{ERS}_{ij_0} \left\{ \sum_{j_1=1}^{k_c} \alpha_{j_1} p_{j_1} \text{EX}_{ij_1} + \sum_{j_1=1}^{k_s} \alpha_{k_c + j_1} q_{j_1} \text{EXS}_{ij_1} \right\} \quad (34)$$

Now we consider the Marquardt procedure <sup>1,2)</sup> in the space of

$$\beta = (p_1, \dots, p_{k_{cv}}, q_1, \dots, q_{k_{sv}}, \theta_0)^T = (p, q, \theta_0)^T \quad (35)$$

for minimizing  $\phi = \sum_i w_i [y_i - f(x_i; \beta)]^2$  for variation of  $\beta$  without constraints [ $f(x_i; \beta)$  is an abbreviation for  $f(x_i; \alpha(\beta); \beta)$ ].

This method is derived from the familiar Gauss-Newton iteration technique by addition of positive terms to the elements of the diagonal of the matrix A corresponding to the system of "normal equations"

$$Ad = g \quad (36)$$

A stands for  $P^T W P$ . P, W, and g have the elements

$$p_{ij} = \frac{\partial f_i}{\partial \beta_j}, \quad w_{ii} = \delta_{ii}, \quad \text{and}$$

$$g_j = \sum_{i=1}^n w_i (y_i - f_i) \frac{\partial f_i}{\partial \beta_j} \quad (j \leq k_\beta).$$

$\beta = (\beta_1, \dots, \beta_{k_v})^T$  refers to a guessed or previously iterated non-linear parameter vector. d is the resulting correction vector to  $\beta$ . The Marquardt modification of (36) reads

$$(A + \lambda D^2) d = g \quad (37)$$

D is a diagonal matrix with its elements scaled according to A,  $d_{ij} = \delta_{ij} (a_{ij})^{-1/2}$ . The additional parameter,  $\lambda$ , that is at our disposal provides for interpolation between the Gauss-Newton method

( $\alpha=0$ ) and a gradient-like method ( $\alpha = \infty$ ). Details in Marquardt's iterative strategy are given elsewhere <sup>1,2,3</sup>.

To set up eq. (37) we shall need the elements  $p_{ij} = \frac{\partial f_i}{\partial \beta_j}$  of P. From  $\alpha=\alpha(\beta)$  is obtained

$$\frac{\partial f_i}{\partial \beta_{j'}} = \sum_{j_1=1}^k \left[ \frac{\partial \alpha_{j_1}}{\partial \beta_{j'}} u_{ij_1} + \alpha_{j_1} \frac{\partial u_{ij_1}}{\partial \beta_{j'}} \right] \quad (j' \leq k_\beta) \quad (38)$$

The derivatives  $\frac{\partial u_{ij}}{\partial \beta_{j'}}$  are given by:

- 1)  $j \leq k_c, j' \leq k_{cv} : \delta_{jj'}, \text{TEX}_{ij}$
- 2)  $j \leq k_c, j' = k_{cv} + j'' : 0$
- 3)  $j \leq k_c, j' = k_\beta : -p_j \text{EX}_{ij} \quad (39)$
- 4)  $j = k_c + j_0, j' \leq k_{cv} : 0$
- 5)  $j = k_c + j_0, j' = k_{cv} + j'' : \delta_{j_0 j''} \text{TEXS}_{ij_0}$
- 6)  $j = k_c + j_0, j' = k_\beta : -q_{j_0} \text{EXS}_{ij_0}$

#### 4. Statistical Analysis

In this section are given the results of a statistical analysis<sup>2)</sup> of the least-squares problems with constraints of the present type. This analysis assumes

- (i) an ideal model
- (ii) small fluctuations of the data ordinates  
(count numbers) around their means.
- (iii) "statistical weighting"

Concerning (i) we know that model (2) is not an ideal model. We have no general theory which indicates that the measured curves can be represented by the model. However, experiments have shown that in many cases parts of the curves or the whole curve can be fitted well by use of one or several Gaussian curves.

(ii) is justified if the total number of counts in the spectrum is sufficiently large. This is generally true in this application.

(iii) concerns the choice of the weights,  $w_i$ , of the data points in the expression for  $\phi$  (eq(12)). These have hitherto been regarded as arbitrary coefficients, but several advantages will be gained<sup>2)</sup> if the so-called statistical weighting is chosen,

$$w_i = \frac{1}{\sigma_i^2} \quad (40)$$

$\sigma_i^2$  is the variance of the  $i$ th data ordinate  $y_i$  and is estimated by the auxiliary program PAAC. With assumptions (i)- (iii) it is possible<sup>2)</sup> to compute the covariance matrix,  $Q$ , of the statistical variable  $b$  [the vector that minimizes (12)]. The result is that  $Q$  is obtained by deletion of the last  $m$  [ cf (14) ] rows and columns from the inverse of the matrix

$$H = \begin{matrix} & k & m \\ \begin{matrix} k \\ m \end{matrix} & \begin{bmatrix} A & | & R^T \\ \hline R & | & \theta \end{bmatrix} \end{matrix} \quad (41)$$

Here, the matrix  $A = p^T W p$  refers to all  $k = k_\alpha + k_\beta$  parameter components (in contrast to  $A$  for the  $\beta$ -iterations, eq. (36)), so in this case  $P$  is an  $n \times k$  matrix with the elements  $P_{ij} = \frac{\partial f_i}{\partial b_j}$ .  $R$  is related to

the set of general constraints

$$k_\ell(b) = 0 (\ell=1, \dots, m) \quad (42)$$

by  $r_{\ell j} = \frac{\partial K_\ell}{\partial b_j}$ . In the present case  $R$  becomes an extension of  $K$

(cf. (22) and (23)),

$$R = \begin{matrix} & k_\alpha & k_\beta \\ \begin{matrix} m \end{matrix} & \begin{bmatrix} K & | & \theta \end{bmatrix} \end{matrix} \quad (43)$$

In the special case of no constraints,  $Q = A^{-1}$ .

We want to express the parameters as well as the associated statistics in terms of relative intensities

$$i_j = \frac{\alpha_j}{\sum_{j=1}^{\alpha} \alpha_j} \quad (44)$$

and fwhm (eqs(5)). The new parameter vector

$b_1 = (i_1, \dots, i_{k_\alpha}, \theta_1, \dots, \theta_{k_{cv}+k_{sv}}, \theta_0)^t$ , where  $\theta$  has been written





## 5. Description of the Code PAACFIT

### 5.1 Structure

The Fortran program PAACFIT (AEK P-673) consists of a driver program and the subroutines GAUSFT, DISP, COLDEC, and COLSOL.

The driver program contains all the input and most of the output instructions. It carries out all the statistical analysis.

GAUSFT is the iterative least-squares fitting routine. It passes to the driver program converged values of the model parameters.

DISP produces a table with data as well as fit ordinates and a lineprinter display of the deviations.

COLDEC and COLSOL are used in the solution of linear systems with symmetric matrices and for inversion of such matrices. COLDEC performs an extended Cholesky decomposition, and COLSOL solves the system on the basis of this decomposition. The two subroutines are called from the driver program during the statistical calculations, and from GAUSFT.

### 5.2 Input

All input data are read from punched cards. The data are divided into five consecutive blocks.

BLOCK1 is a single card containing the word JOB and a job number, IJOB. The format is A3,I7. If "JOB" is not recognized, an error message is printed. IJOB<0 signals the end of the job stream.

BLOCK2 is a single card containing the print-out option IPRINT, format I 10. IPRINT=0 causes print-out of the main results. IPRINT=1 gives in addition a print-out of the parameters at each iteration, and IPRINT=2 furthermore a table with data as well as fit ordinates and a graphical display of the deviations.

BLOCK3 is a single card containing the length of the table N, format I10.

BLOCKS 4 and 5 both start with a text card with one of the words NEW or REP, format A3. If the card is a REP card, this will be the entire contents of that block, and the corresponding block data from the previous job are repeated. If neither "NEW" or "REP" is recognized, an error message occurs.

BLOCK4 contains the spectrum data. The first card after a NEW card is a text card with a description of the spectrum (col. 1-72). The next items are the angle table (X(I), I=1,N), format 10F8.2; the count-rate table (Y(I), I=1,N), format 16F5.0; and the standard-deviation table (SIGMA(I), I=1,N), format 16F5.0. These tables constitute the punched output from the PAAC program. (cf.(1), sec. 2).

BLOCK5 contains information on number of terms, parameter guesses and constraints. The first card after a NEW card holds the five integers KC, KS, KCF, KSF, M, format 5I10. KC is the number of central peaks, KS the number of sidepeak pairs in the model. Of these, KCF central fwhm and KSF sidepeak fwhm are fixed. |M| is the number of constraints on the intensities. If KS>0, a card follows with the sidepeak positions, format 2E10.5. The next card contains all the KC initial values (guessed followed by fixed) of the central fwhm, format 5E10.5. If KS>0, a card follows with the KS initial values (guessed followed by fixed) of the sidepeak fwhm, format 2E10.5. The next card holds the guessed value for the angle-zero  $\theta_0$ , format E10.5. If M>0, M of the relative intensities are fixed. In this case, the next data item is a pair of cards with the numbers (JL(L), L=1,..., M) and (RINTF(L), L=1,..., M), format 6I10/6E10.5; JL(L) is the term no. associated with constraint no. L (the numbering of terms is defined from the previous card(s) with the central fwhms followed by the sidepeak fwhms), and RINTF(L) is the corresponding fixed relative intensity in percent. If M<0, |M| linear combinations of the absolute intensities equal zero,

$$\sum_{j=1}^{KC+KS} k_{lj} \alpha_j = 0;$$

in this case the next data item contains |M| cards so that card number  $l$  holds the coefficients  $k_{lj}$  with the identifier COMB (J,L) (J=1,..., KC+KS), format 7E10.5. The option M<0 may be used to fix ratio between intensities or the sum of certain relative intensities.

Restrictions on the input data in the present version (1/7 1973) of PAACFIT are:  $N \leq 100$ ,  $0 < KC \leq 5$ ,  $0 \leq KS \leq 2$ ,  $0 \leq |M| < KC + KS$ ,  $0 \leq KCF \leq KC$ ,  $0 \leq KSF \leq KS$ .

## 6. Experience with the Program.

The program has until now been used in about 500 analyses of more than 100 different angular correlation curves. Most of the results will be published in detail in other papers. In figures 1 and 2 are shown some of the curves. These figures were computer-plotted by use of the program PAACDRAW. The fitting parameters of the curves, determined by the PAACFIT analyses, are given in table 1 and the fitting curves are plotted in the figures.

As mentioned earlier (sec 4) we normally have no theory indicating that the model is ideal. In practice, however, we frequently measure curves which, wholly or in part, can be fitted well by one Gaussian (e.g. the broad component of many metal curves). Our experience is that we have been able to fit well all the curves we have analysed. In a typical case of a bell-shaped curve with no sidepeaks a one -Gaussian fit is rather bad, a two-Gaussian fit is fairly reasonable, and three Gaussians fit very well with parameters that are already not too well determined (see the cystine parameters in table 1.) A four-Gaussian fit will normally be so uncertain that much computing time is used and some of the fitting parameters attain unacceptable values (e.g. intensities of thousands of percent or very large fwhm's). We want to emphasize that the model can contain so many fitting parameters that a good fit can nearly always be obtained, and thus extreme care must be exercised in the final correlation of the parameters to some physical quantities.

Before we used the program for analysis of the measured curves we analysed some calculated curves. For example we analysed a calculated curve with a shape close to the shape of the a-axis ice curve. The program found the same intensities and fwhm's as used in the calculation, except for the fwhm's of the very narrow central and side peaks, where the program found 0.7815 instead of 0.8 mrad and 0.5749 mrad instead of 0.6 mrad respectively. This very small error arises because the measured numbers  $y_i$  are compared to interval averages for the model curve in the fitting procedure (cf. sec. 3) It can be reduced if more points are measured on the narrow peaks. We have also tested the program many times by e.g.

varying the initial guesses of the fwhm's or by analysing different curves measured for identical sample conditions.

A more detailed discussion of a series of analyses of the a-axis ice curves will illustrate some of the problems we encountered in the fitting procedures. At low temperatures the curves consisted of a broad component, a narrow component, and a sidepeak pair, while at higher temperatures also a middle-broad component was found. We wanted especially to get good values for the intensities of the narrow central and side peaks (due to annihilation of delocalized para-positronium (para Ps)) and of the middlebroad component (due to localized para-Ps). At first we analysed nearly all the a-axis curves by use of three central Gaussians and one pair of side-peak Gaussians. The side-peak positions were calculated by use of the ice lattice parameters. The fitting was good, but for many of the curves the values of the fitting parameters were not acceptable. For example the fwhm's of the side peaks sometimes attained values of 5 to 10 mrad at some of the highest temperatures, where the side peaks were rather small. For the a-axis - 182°C curve (see fig. 1) the broad component was well fitted by two Gaussians (84.6757% with fwhm = 10.3941 mrad and - 1.0130% with fwhm = 5.8701 mrad). A one-Gaussian fit of the broad component was rather bad and three Gaussians did not give a smaller variance of the fit.

We then analysed the curves by use of four central Gaussians and a pair of side-peak Gaussians. The shape of the broad component was fixed to the shape found at -182°C by use of fixed fwhm's (fwhm<sub>1</sub> = 5.8701 mrad and fwhm<sub>2</sub> = 10.3941 mrad) and one linear - combination - of-intensities constraint,  $84.6757 \times i_1 + 1.013 \times i_2 = 0$ . Again the parameters for some of the higher temperature curves were unacceptable. The reason was that the larger angle parts of the curves strongly influenced the intensity of the broad component, and hence the side peaks and middle-broad component were to some extent used to compensate a too small or a too large broad component at smaller angles.

From theory we expected that the broad component would be approximately independent of temperature except for a small correction of the intensity. This was found to be roughly in agreement with the results of the first analyses. We therefore analysed the

curves by use of four central Gaussians and one pair of side - peak Gaussians with the broad component fixed to the shape used before and an intensity calculated by use of lifetime data. The parameters were now fairly acceptable but for some curves they were still somewhat too uncertain. We analysed once more using fixed side-peak fwhm's with a theoretical temperature dependence. The fwhm's for the middle-broad curves for temperatures above  $-40^{\circ}\text{C}$ , where the middle-broad components were well defined, were then found to be very constant. For 11 curves we found  $\text{fwhm}_2 = 3.94 \pm 0.09 \text{ mrad}$ .

In the final analyses we therefore also fixed  $\text{fwhm}_2$  to be 3.94 mrad. This gave a variance of the fit close to the best values obtained in the analyses, where all the parameters were free, and the parameters, which were free to vary, were well defined. The ice curves for other orientations and for HF-doped ice were treated similarly. Manual treatments of some of the curves have been published in ref. 5. The ice curves given in Fig. 1 and table 1 are the results of the final analysis. The complete lineprinter output for curve 1 (c-axis,  $-181^{\circ}\text{C}$ ) is shown as the test run output in appendix 2.

In Fig. 2 (see also table 1) are shown curves for cystine, acetylmethionine and  $\gamma$ -irradiated (30 Mrad) acetylmethionine. In acetylmethionine  $\gamma$ -irradiation reduces the amount of Ps formed. Para-Ps annihilation results in a middle-broad component in the angular correlation curves. We assumed that the rest of acetylmethionine curves, the broad component, had the same shape as the cystine curve, where no Ps is formed. For the cystine curve three Gaussians were necessary to give a good fit. Hence, we analysed the acetylmethionine curves by use of four Gaussians, one for the middle-broad component and three to fit the broad component, using two linear - combination - of - intensities constraints and fixed fwhm's to fix the shape of the broad component to the shape of cystine curve. The intensities of the middle-broad curves in Fig. 2 and table 1 therefore give the amount of para-Ps formed. A manual treatment of the same curves have been published in ref. 6. This example illustrates how a curve may be separated into two parts, of which one has a fixed shape, by use of the linear - combination -

of - intensities constraints.

In sec. 4 it was pointed out, that on the assumption of an ideal model, the distribution of the "variance of the fit",  $s^2$  (cf.(47)), should be approximately normal with mean value 1 and with s.d.  $= \sqrt{\frac{2}{q}} \approx 0.17$  (in our application  $q$  was always near 70). Except for a very few cases we found much larger values, typically about 4. The reason is of course that the model is not ideal. Firstly, the curves cannot always be fitted by use of only Gaussians. Secondly, the curves contain small errors due to different experimental effects. For example, the narrow peaks are not completely symmetrical because of a small asymmetry of the resolution curve of the set-up owing to the variation of the position-penetration depth of the ice sample. The curves measured with the smallest statistical counting uncertainties gave the largest  $\Phi$  - values, as expected.

The computing time on a Burroughs B 6700 was roughly 10 to 20 seconds, this corresponds roughly to 1-2 sec. on an IBM 370/165, depending on the number of points in the curves (typically around 75) and on the constraints used. The number of iterations to obtain convergence was usually of the order of 14 for unconstrained fits and around 7 for heavily constrained fits.

We conclude that the program is a very useful tool for the analysis of angular correlation curves. It may of course also be used for the analysis of symmetrical curves obtained in other experiments (e.g. the resolution curve of a positron lifetime set-up). As the program can handle negative intensities, curves of many different shapes can be analysed. In particular the possibility of using different constraints in the analysis has been found to be very applicable. The main problems of an analysis is to use the constraints in an intelligent way in order that the fitting parameters can be correlated unambiguously to the physical quantities. In other words, it is nearly always possible to obtain a good fit, but it may be very difficult to make out the meaning of the fitting parameters.

## 7. References

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- 2) P. Kirkegaard, Some Aspects of the General Least-Squares Problem for Data Fitting, Risø-M-1399 (1971).
- 3) P. Kirkegaard and M. Eldrup, POSITRONFIT: A Versatile Program for Analysing Positron Lifetime Spectra. Computer Physics Comm. 3 (1972) 240-255.
- 4) P. Kirkegaard and M. Eldrup, The Least-Squares Fitting Programme POSITRONFIT: Principles and Formulas, Risø-M-1400 (1971)
- 5) O. Mogensen and M. Eldrup, Proc. Conf. Phys. Chem. Ice, Ottawa (1972), to be published.
- 6) M. Eldrup, E. Lund-Thomsen, and O. Mogensen, J. Chem. Phys. 56, 4902 (1972).

Appendix 1: Test run input

```

JNB      5
          2
          77
NEW
H2O-C-1.S1  T=-18C.9'C
-12.74 -12.11 -11.48
-7.00 -6.82 -6.57
-4.10 -3.93 -3.67
-1.72 -1.53 -1.34
0.17 0.36 0.55
2.25 2.50 2.75
5.14 5.40 5.65
8.54 9.17 9.80
183 240 394 510 747
4588 5010 5443 5793 6289
9477 95701050812104157032086626839303022820422563158511214110376
8927 8762 8408 8373 8175 7917 7682 7350 6834 6485 6037 5581 5013 4746 4479 4097
4089 4041 3993 3585 2701 2038 1460 1151 871 643 460 319 194
13 15 19 21 26 32 34 40 46 50 53 58 62 60 62
64 67 70 72 75 78 80 83 84 85 86 87 88 89 92
100 93 98 105 111 138 156 166 160 143 130 105 97 93 92 92
90 89 88 87 86 85 84 82 85 77 80 71 68 71 64 61
61 72 60 57 55 43 40 32 28 24 22 17 16
NEW
          3      2      2      2
3.315      6.630
1.         3.70      10.5)
0.950      0.950
0.00
83.660      0.559
JNB      -1

```



# Appendix 2: Test run output

JOB NO 5

X-TABLE

|        |        |        |        |        |       |       |       |       |       |
|--------|--------|--------|--------|--------|-------|-------|-------|-------|-------|
| -12.74 | -12.11 | -11.48 | -10.85 | -10.22 | -9.59 | -8.96 | -8.34 | -7.71 | -7.08 |
| -7.06  | -6.42  | -5.79  | -5.16  | -4.53  | -3.90 | -3.27 | -2.64 | -2.01 | -1.38 |
| -1.74  | -1.09  | -0.46  | 0.17   | 0.80   | 1.43  | 2.06  | 2.69  | 3.32  | 3.95  |
| 4.58   | 5.21   | 5.84   | 6.47   | 7.10   | 7.73  | 8.36  | 8.99  | 9.62  | 10.25 |
| 10.88  | 11.51  | 12.14  | 12.77  | 13.40  | 14.03 | 14.66 | 15.29 | 15.92 | 16.55 |
| 17.18  | 17.81  | 18.44  | 19.07  | 19.70  | 20.33 | 20.96 | 21.59 | 22.22 | 22.85 |
| 24.08  | 24.71  | 25.34  | 25.97  | 26.60  | 27.23 | 27.86 | 28.49 | 29.12 | 29.75 |
| 31.64  | 32.27  | 32.90  | 33.53  | 34.16  | 34.79 | 35.42 | 36.05 | 36.68 | 37.31 |
| 40.56  | 41.19  | 41.82  | 42.45  | 43.08  | 43.71 | 44.34 | 44.97 | 45.60 | 46.23 |

Y-TABLE

|       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 183   | 240   | 304   | 376   | 457   | 548   | 649   | 760   | 881   | 1012  |
| 1153  | 1294  | 1445  | 1606  | 1777  | 1958  | 2149  | 2350  | 2561  | 2782  |
| 3013  | 3244  | 3485  | 3736  | 4007  | 4288  | 4579  | 4880  | 5191  | 5512  |
| 5843  | 6174  | 6515  | 6866  | 7227  | 7598  | 7979  | 8370  | 8771  | 9182  |
| 9603  | 10044 | 10495 | 10956 | 11427 | 11908 | 12399 | 12900 | 13411 | 13932 |
| 14463 | 14984 | 15505 | 16026 | 16547 | 17068 | 17589 | 18110 | 18631 | 19152 |
| 19673 | 20194 | 20715 | 21236 | 21757 | 22278 | 22799 | 23320 | 23841 | 24362 |
| 24883 | 25404 | 25925 | 26446 | 26967 | 27488 | 28009 | 28530 | 29051 | 29572 |
| 30093 | 30614 | 31135 | 31656 | 32177 | 32698 | 33219 | 33740 | 34261 | 34782 |

SIGMA-TABLE

|        |        |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 13     | 15     | 17     | 21     | 25     | 32     | 40     | 50     | 63     | 80     |
| 100    | 120    | 140    | 170    | 210    | 260    | 330    | 430    | 570    | 760    |
| 1000   | 1200   | 1400   | 1700   | 2100   | 2600   | 3300   | 4300   | 5700   | 7600   |
| 10000  | 12000  | 14000  | 17000  | 21000  | 26000  | 33000  | 43000  | 57000  | 76000  |
| 100000 | 120000 | 140000 | 170000 | 210000 | 260000 | 330000 | 430000 | 570000 | 760000 |

INITIAL VALUES OF NONLINEAR PARAMETERS  
CENTRAL FWHMS (FIRST TWOSE TO BE FITTED)  
1.00000E+00 3.70000E+00 1.05000E+01  
SIDEPEAK FWHMS (FIRST TWOSE TO BE FITTED)  
0.50000E-01 0.50000E-01  
THETA=0.0000  
0.0000

ITERATION NO 1

SHARPNESS OF CENTRAL PEAKS

1.00000E+01

THETA0

0.0

INTENSITY OF CENTRAL PEAKS

2.00000E+05 1.99700E+04 1.00000E+06

INTENSITY OF SIDEPEAKS

7.40000E+03 1.03277E+04

PHI = 0.00000E+00

KAPPA = 0.0000E-01

A

ITERATION NO 2

SHARPNESS OF CENTRAL PEAKS

1.00000E+01

THETA0

0.00000E+00

INTENSITY OF CENTRAL PEAKS

1.00000E+05 1.99700E+04 1.00000E+06

INTENSITY OF SIDEPEAKS

7.40000E+03 1.03277E+04

PHI = 0.00000E+00

KAPPA = 0.0000E-02

A

ITERATION NO 3

SHARPNESS OF CENTRAL PEAKS

1.00000E+01

THETA0

0.00000E+00

INTENSITY OF CENTRAL PEAKS

1.00000E+05 1.99700E+04 1.00000E+06

INTENSITY OF SIDEPEAKS

7.40000E+03 1.03277E+04

PHI = 0.00000E+00

KAPPA = 0.0000E-03

A

ITERATION NO 4

SHARPNESS OF CENTRAL PEAKS

1.00000E+01

THETA0

0.00000E+00

INTENSITY OF CENTRAL PEAKS

1.00000E+05 1.99700E+04 1.00000E+06

INTENSITY OF SIDEPEAKS

7.40000E+03 1.03277E+04

PHI = 0.00000E+00

KAPPA = 0.0000E-04

A

ITERATION NO 5

SHARPNESS OF CENTRAL PEAKS

1.00000E+01

THETA0

0.00000E+00

INTENSITY OF CENTRAL PEAKS

1.00000E+05 1.99700E+04 1.00000E+06

INTENSITY OF SIDEPEAKS

7.40000E+03 1.03277E+04

PHI = 0.00000E+00

KAPPA = 0.0000E-05

A

ITERATION NO 6

SHARPNESS OF CENTRAL PEAKS

1.00000E+01

THETA0

0.00000E+00

INTENSITY OF CENTRAL PEAKS

1.00000E+05 1.99700E+04 1.00000E+06

INTENSITY OF SIDEPEAKS

7.40000E+03 1.03277E+04

PHI = 0.00000E+00

KAPPA = 0.0000E-06

A

\*\*\*\*\*  
 n20=C-1.51 T=-140.9'C  
 \*\*\*\*\*

CONVERGENCE OBTAINED AFTER 6 ITERATIONS  
 VARIANCE OF THE FIT = 2.053  
 ITS DISTRIBUTION SHOULD BE APPROXIMATELY NORMAL (1.0,167)  
 EXCESS PROBABILITY = 0.00 PCT

NUMBER OF CENTRAL PEAKS = 3                      NUMBER OF SIDEPEAK PAIRS = 2  
 NUMBER OF FIXED CENTRAL FWHM = 2              NUMBER OF FIXED SIDE FWHM = 2

NUMBER OF CONSTRAINTS FOR RELATIVE INTENSITIES = 2  
 FIXED RELATIVE INTENSITIES FOR PEAKS NO                      3                      4  
 PERCENTUAL INTENSITIES                      83.6600                      0.5590

POSITION OF SIDEPEAKS              3.3150      6.6300

LENGTH OF TABLE = 77

|                                      |         |        |         |
|--------------------------------------|---------|--------|---------|
| INTENSITIES OF CENTRAL PEAKS IN PCT  | 14.5594 | 0.0542 | 83.6600 |
| STANDARD DEVIATIONS                  | 0.0888  | 0.0965 | 0.0000  |
| INTENSITIES OF SIDEPEAK PAIRS IN PCT | 0.5590  | 1.1674 |         |
| STANDARD DEVIATIONS                  | 0.0000  | 0.0377 |         |
| FWHM FOR CENTRAL PEAKS               | 0.8614  | 3.7000 | 10.5900 |
| STANDARD DEVIATIONS                  | 0.0048  |        |         |
| FWHM FOR SIDEPEAK PAIRS              | 0.9500  | 0.9500 |         |
| ANGLE=ZERO THETA0 (MRAD)             | -0.0063 |        |         |
| STANDARD DEVIATION                   | 0.0018  |        |         |

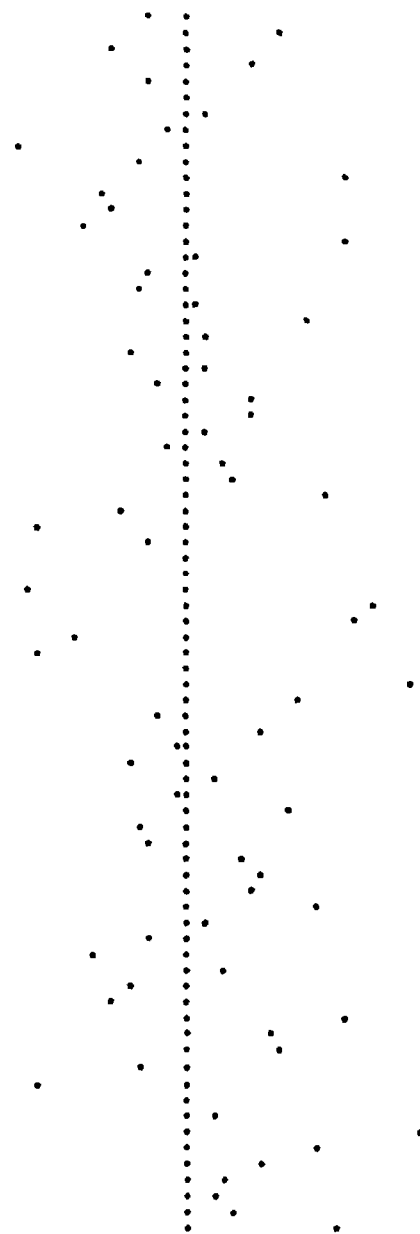
AREA CHECK      AREA FROM FIT = 1.29511E+05  
                   AREA FROM TABLE = 1.29416E+05

MATRIX OF TOTAL CORRELATIONS  
 (RELATIVE INTENSITIES, FREE FWHMS, THETA0)

|        |        |       |       |        |        |        |
|--------|--------|-------|-------|--------|--------|--------|
| 1.000  | -0.921 | 0.000 | 0.000 | -0.001 | 0.615  | -0.014 |
| -0.921 | 1.000  | 0.000 | 0.000 | -0.390 | -0.595 | 0.016  |
| 0.000  | 0.000  | 0.000 | 0.000 | 0.000  | 0.000  | 0.000  |
| 0.000  | 0.000  | 0.000 | 0.000 | 0.000  | 0.000  | 0.000  |
| -0.001 | -0.390 | 0.000 | 0.000 | 1.000  | 0.073  | -0.008 |
| 0.615  | -0.595 | 0.000 | 0.000 | 0.073  | 1.000  | -0.011 |
| -0.014 | 0.016  | 0.000 | 0.000 | -0.008 | -0.011 | 1.000  |

| X       | TABLE Y    | FIT Y      |
|---------|------------|------------|
| -12.740 | 1.8300E+02 | 1.7514E+02 |
| -12.110 | 2.4000E+02 | 2.5741E+02 |
| -11.480 | 3.0600E+02 | 3.7400E+02 |
| -10.850 | 3.1700E+02 | 5.2715E+02 |
| -10.220 | 7.6700E+02 | 7.3415E+02 |
| -9.590  | 9.9900E+02 | 9.9301E+02 |
| -8.960  | 1.3210E+03 | 1.3310E+03 |
| -8.340  | 1.7460E+03 | 1.7301E+03 |
| -7.710  | 2.3000E+03 | 2.1999E+03 |
| -7.080  | 2.7230E+03 | 2.6391E+03 |
| -6.450  | 3.1660E+03 | 3.2107E+03 |
| -5.820  | 3.7690E+03 | 3.7253E+03 |
| -5.190  | 4.1200E+03 | 4.0549E+03 |
| -4.560  | 4.2300E+03 | 4.1694E+03 |
| -3.930  | 4.0500E+03 | 4.1716E+03 |
| -3.300  | 4.2700E+03 | 4.2809E+03 |
| -2.670  | 4.5680E+03 | 4.5553E+03 |
| -2.040  | 5.0100E+03 | 4.9649E+03 |
| -1.410  | 5.4430E+03 | 5.4538E+03 |
| -0.780  | 5.7730E+03 | 5.9123E+03 |
| -0.150  | 6.2890E+03 | 6.3104E+03 |
| 0.480   | 6.7730E+03 | 6.7153E+03 |
| 1.110   | 7.1420E+03 | 7.1651E+03 |
| 1.740   | 7.6120E+03 | 7.5767E+03 |
| 2.370   | 7.7910E+03 | 7.8642E+03 |
| 3.000   | 7.9670E+03 | 8.0541E+03 |
| 3.630   | 8.1800E+03 | 8.2300E+03 |
| 4.260   | 8.4190E+03 | 8.3951E+03 |
| 4.890   | 8.5730E+03 | 8.6190E+03 |
| 5.520   | 8.7480E+03 | 8.8190E+03 |
| 6.150   | 8.8100E+03 | 8.9909E+03 |
| 6.780   | 9.2140E+03 | 9.1233E+03 |
| 7.410   | 9.4770E+03 | 9.2740E+03 |
| 8.040   | 9.5700E+03 | 9.5182E+03 |
| 8.670   | 1.0900E+04 | 1.0130E+04 |
| 9.300   | 1.2100E+04 | 1.1810E+04 |
| 9.930   | 1.5700E+04 | 1.5400E+04 |
| 10.560  | 2.0860E+04 | 2.1212E+04 |
| 11.190  | 2.6839E+04 | 2.7193E+04 |
| 11.820  | 3.0302E+04 | 3.0300E+04 |
| 12.450  | 2.8204E+04 | 2.7874E+04 |
| 13.080  | 2.2563E+04 | 2.2131E+04 |
| 13.710  | 1.5851E+04 | 1.6230E+04 |
| 14.340  | 1.2141E+04 | 1.2304E+04 |
| 14.970  | 1.0376E+04 | 1.0345E+04 |
| 15.600  | 9.6920E+03 | 9.5817E+03 |
| 16.230  | 9.3880E+03 | 9.2999E+03 |
| 16.860  | 9.1980E+03 | 9.1325E+03 |
| 17.490  | 8.9270E+03 | 8.9552E+03 |
| 18.120  | 8.7420E+03 | 8.7483E+03 |
| 18.750  | 8.4080E+03 | 8.5240E+03 |
| 19.380  | 8.3730E+03 | 8.3130E+03 |
| 20.010  | 8.1760E+03 | 8.1376E+03 |
| 20.640  | 7.9170E+03 | 7.9336E+03 |
| 21.270  | 7.6820E+03 | 7.7707E+03 |
| 21.900  | 7.3500E+03 | 7.4242E+03 |
| 22.530  | 6.8340E+03 | 6.9867E+03 |
| 23.160  | 6.4850E+03 | 6.5353E+03 |
| 23.790  | 6.0370E+03 | 5.9946E+03 |
| 24.420  | 5.5810E+03 | 5.4926E+03 |
| 25.050  | 5.0130E+03 | 5.0484E+03 |
| 25.680  | 4.7460E+03 | 4.6952E+03 |
| 26.310  | 4.4790E+03 | 4.4180E+03 |
| 26.940  | 4.0970E+03 | 4.2274E+03 |
| 27.570  | 4.0890E+03 | 4.1588E+03 |
| 28.200  | 4.0410E+03 | 4.1330E+03 |
| 28.830  | 3.9930E+03 | 3.9540E+03 |
| 29.460  | 3.5050E+03 | 3.4683E+03 |
| 30.090  | 2.7010E+03 | 2.6985E+03 |
| 30.720  | 2.0380E+03 | 2.0554E+03 |
| 31.350  | 1.6800E+03 | 1.5871E+03 |
| 31.980  | 1.1510E+03 | 1.2361E+03 |
| 32.610  | 8.7100E+02 | 8.9764E+02 |
| 33.240  | 6.4300E+02 | 6.5539E+02 |
| 33.870  | 4.6000E+02 | 4.6912E+02 |
| 34.500  | 3.1900E+02 | 3.2928E+02 |
| 35.130  | 1.9400E+02 | 2.2644E+02 |

DEFLECTION (FIT=TABLE) IN SIGMA UNITS



CPU TIME = 8.65 SEC. I/O TIME = 1.40 SEC. REAL TIME = 10.02 SEC. REAL/CPU RATIO = 1.26

| Curve No. | Substance           | $i_1$<br>(%)      | $i_2$<br>(%)      | $i_3$<br>(%)      | $i_4$<br>(%)    | $i_5$<br>(%)    | FWHM <sub>1</sub><br>(mrad) | FWHM <sub>2</sub><br>(mrad) | FWHM <sub>3</sub><br>(mrad) | FWHM <sub>4</sub><br>(mrad) | FWHM <sub>5</sub><br>(mrad) | Symmetry angle<br>(mrad) | Variance of the Fit | Remarks              |
|-----------|---------------------|-------------------|-------------------|-------------------|-----------------|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|--------------------------|---------------------|----------------------|
| 1         | ice<br>c-axis       | 14.559<br>±0.089  | 0.054<br>±0.097   | 83.66<br>f        | 0.559<br>f      | 1.167<br>±0.038 | 0.861<br>±0.005             | 3.700<br>f                  | 10.590<br>f                 | 0.950<br>f                  | 0.950<br>f                  | -0.0063<br>±0.0018       | 2.053               | -181° C<br>pure      |
| 2         | ice<br>a-axis       | 13.813<br>±0.077  | 0.007<br>±0.088   | -1.013<br>f       | 84.676<br>f     | 2.517<br>±0.039 | 0.849<br>±0.004             | 3.940<br>f                  | 5.870<br>f                  | 10.394<br>f                 | 0.950<br>f                  | -0.0082<br>±0.0016       | 5.164               | -182° C<br>pure      |
| 3         | ice<br>c-axis       | 10.569<br>±0.074  | 5.060<br>±0.080   | 83.333<br>f       | 0.316<br>f      | 0.722<br>±0.027 | 1.105<br>±0.006             | 3.700<br>f                  | 10.59<br>f                  | 1.081<br>f                  | 1.081<br>f                  | -0.0135<br>±0.0019       | 4.023               | -49° C<br>pure       |
| 4         | ice<br>a-axis       | 6.430<br>±0.065   | 9.367<br>±0.074   | -1.005<br>f       | 83.987<br>f     | 1.221<br>±0.029 | 0.883<br>±0.008             | 3.64<br>f                   | 5.870<br>f                  | 10.394<br>f                 | 0.960<br>f                  | -0.000<br>±0.023         | 6.325               | -177° C<br>23 ppm HF |
| 5         | ice<br>a-axis       | 5.88<br>±0.192    | 10.474<br>±0.209  | -1.004<br>f       | 83.949<br>f     | 0.698<br>±0.068 | 1.251<br>±0.034             | 3.940<br>f                  | 5.870<br>f                  | 10.394<br>f                 | 1.112<br>f                  | 0.0815<br>±0.0067        | 1.602               | -4° C<br>pure        |
| 6         | ice<br>a-axis       | 5.223<br>±0.131   | 11.203<br>±0.145  | -1.004<br>f       | 83.912<br>f     | 0.666<br>±0.044 | 1.224<br>±0.024             | 3.94<br>f                   | 5.87<br>f                   | 10.394<br>f                 | 1.115<br>f                  | -0.0053<br>±0.0045       | 1.745               | -1° C<br>pure        |
| 7         | cystine<br>polycr.  | -16.402<br>±5.979 | 110.393<br>±4.002 | 6.009<br>±2.326   | -<br>-          | -<br>-          | 5.564<br>±0.386             | 8.830<br>±0.216             | 20.566<br>±5.630            | -<br>-                      | -<br>-                      | 0.9167<br>±0.0049        | 1.104               | 20° C<br>non-irr     |
| 8         | acetylm.<br>polycr. | 14.982<br>±0.305  | -13.945<br>±0.050 | 93.854<br>±0.337  | 5.109<br>±0.018 | -<br>-          | 4.128<br>±0.064             | 5.564<br>f                  | 8.830<br>f                  | 20.566<br>f                 | -<br>-                      | 0.7826<br>±0.0069        | 1.820               | 20° C<br>non-irr     |
| 9         | acetylm.<br>polycr  | 8.947<br>±0.266   | -14.935<br>±0.044 | 100.516<br>±0.294 | 5.472<br>±0.016 | -<br>-          | 3.832<br>±0.091             | 5.564<br>f                  | 8.830<br>f                  | 20.566<br>f                 | -<br>-                      | 2.1035<br>±0.0068        | 1.255               | 20° C<br>γ-irr       |

**Table 1** The fitting parameters and their uncertainties as determined by the PAACFIT analyses for all the curves shown in figures 1 and 2. The letter f indicates that the parameter has been fixed.

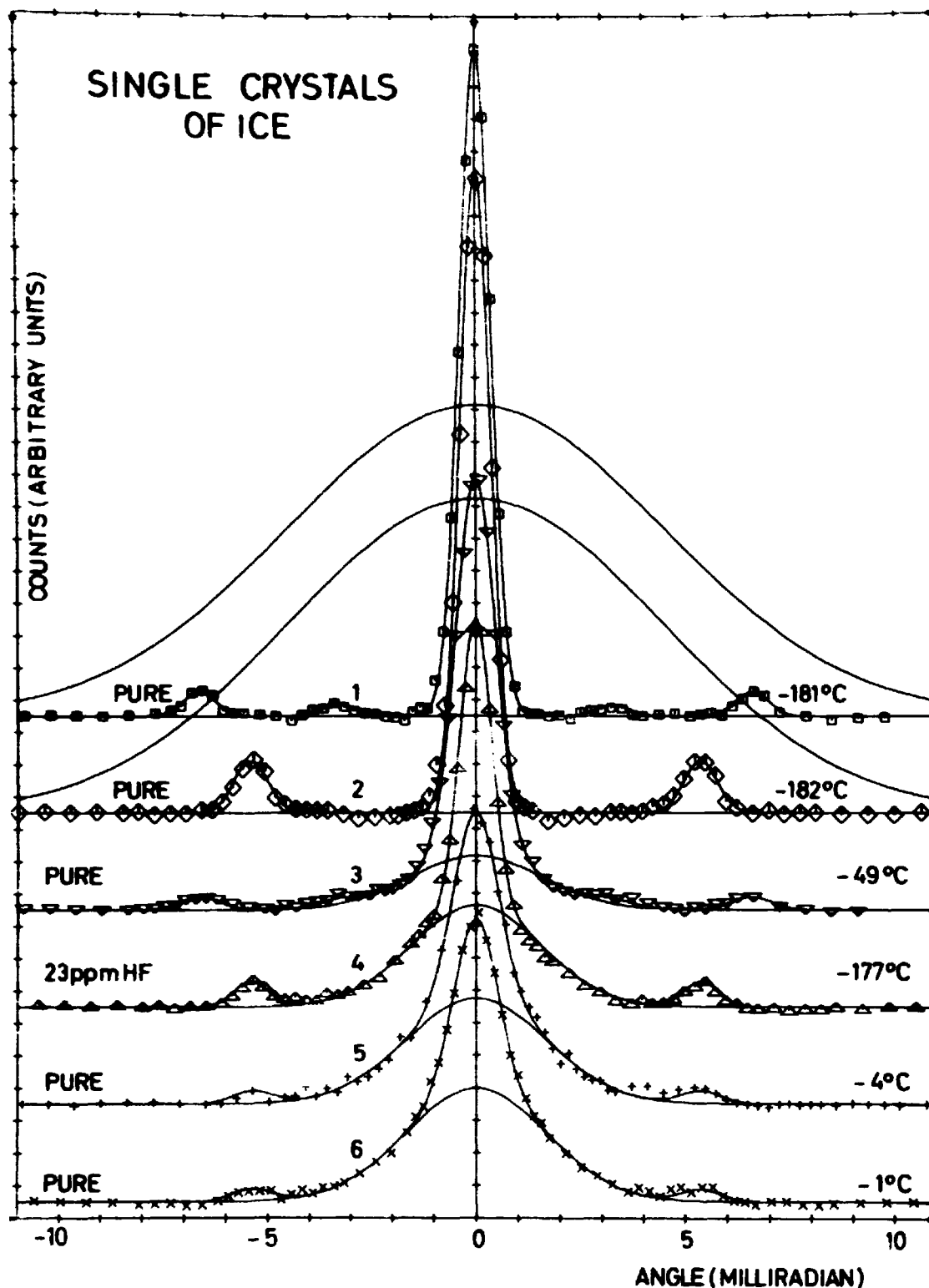


Figure 1. Positron annihilation angular correlation curves for ice single crystals plotted by use of the PAACDRAW-program. The curves are the best fits to the measured points calculated by use of the PAACFIT-program. The points and the fitting curves have been plotted after the subtraction of the broad components, which have been plotted for the a-axis and c-axis low temperature curves. The statistical counting uncertainties are all smaller than roughly the size of the marks. The parameters of the curves are shown in table 1.

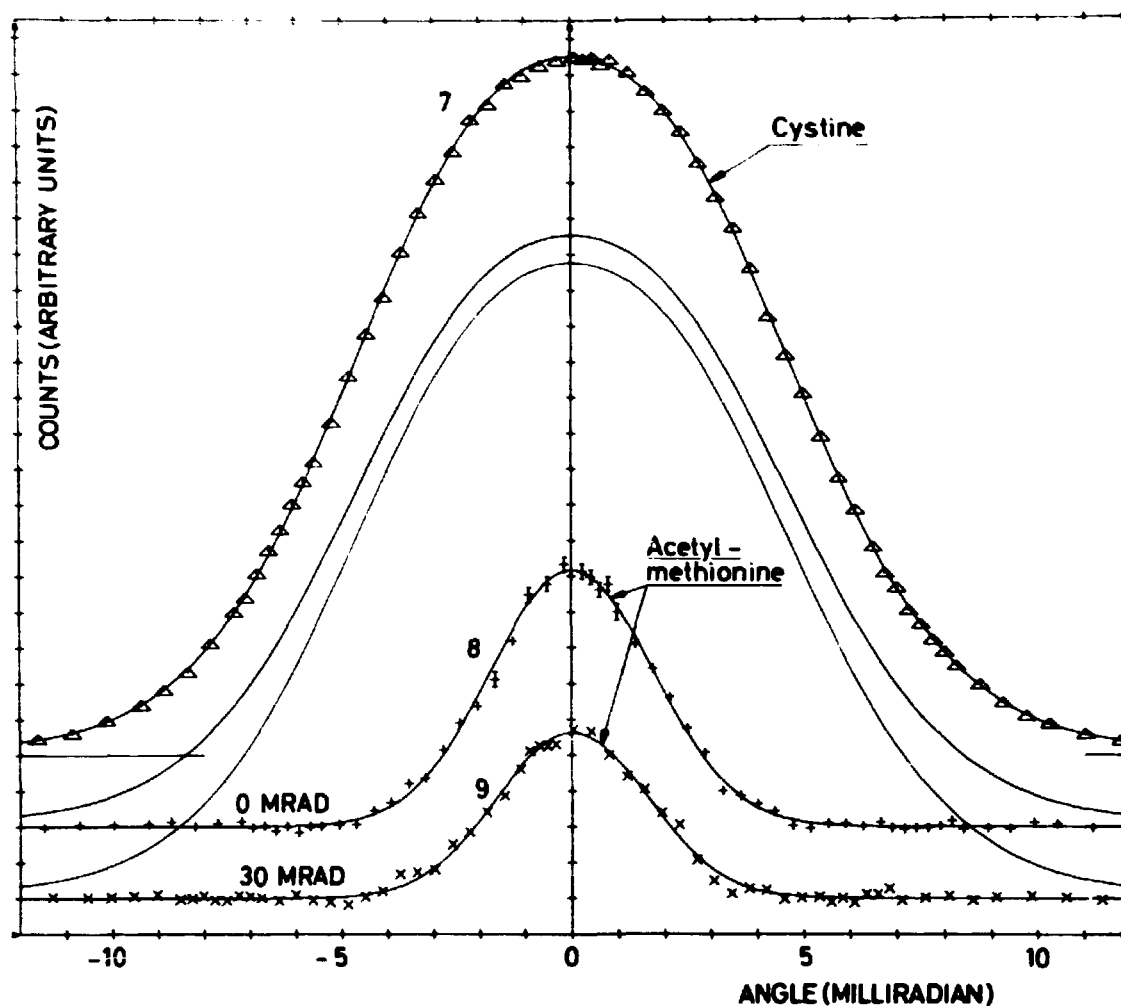


Figure 2. Positron annihilation angular correlation curves for cystine (7), acetylmethionine (8), and  $\gamma$ -irradiated ( $^{60}\text{Co}$ ) acetylmethionine (9) plotted by use of the PAACDRAW-program. The curves are the best fits to the measured points calculated by use of the PAACFIT-program. The two acetylmethionine curves are shown after the subtraction of the broad components (shown in the figure), whose shapes have been fixed to the shape of the cystine curve by use of constraints in the fitting analysis. The statistical counting uncertainties are only shown if they are larger than roughly the size of the marks. The parameters of the curves are shown in table 1.

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